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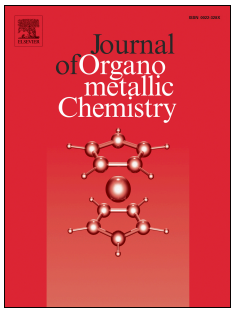

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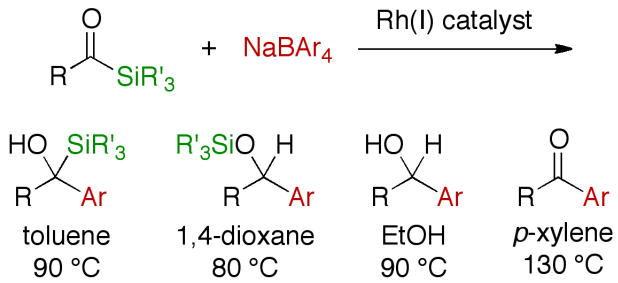
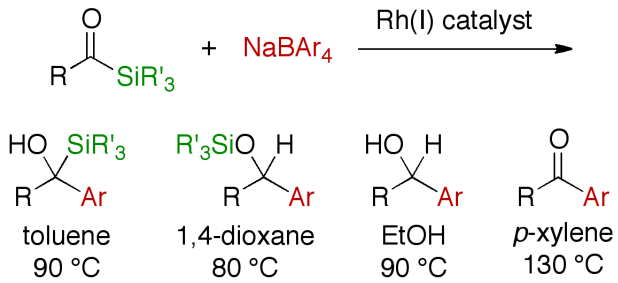


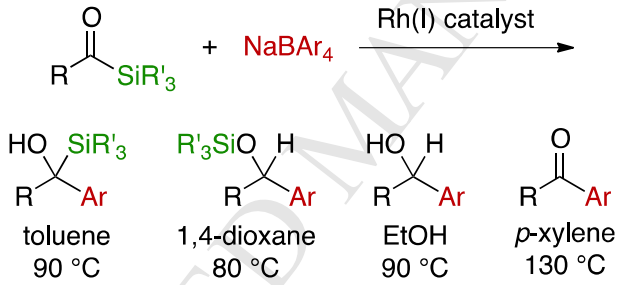


Rhodium-catalyzed arylation of acylsilanes with sodium tetraarylborates

Takanori Matsuda*, Kohei Mizuno, Shoichi Watanuki

Department of Applied Chemistry, Tokyo University of Science, 1–3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

Abstract: Rhodium(I)-catalyzed arylation of benzoylsilanes with sodium tetraarylborates affords α-silyl benzhydrols, benzhydryl silyl ethers, benzhydrols, and diaryl ketones selectively depending on the catalyst, solvent, and temperature.



Keywords: Acylsilane, Addition, Alcohol, Boron, Homogeneous catalysis, Ketone, Rhodium

1. Introduction

Extensive studies have been conducted on rhodium(I)-catalyzed 1,2-addition reactions of arylboron compounds to carbonyl compounds, which has become an indispensable synthetic tool in the preparation of alcohols and ketones [1]. Several classes of carbonyl

* Corresponding author. Fax: +81 3 52614631.

E-mail address: mtd@rs.tus.ac.jp (T. Matsuda).

compounds, including aldehydes [2], ketones [3], esters [4] and acid anhydrides [5], have been identified as viable reaction partners for the rhodium(I)-catalyzed arylation with arylboron compounds. However, to the best of our knowledge, the literature contains no reports of the rhodium(I)-catalyzed arylation of acylsilanes with arylboron compounds [6,7]. We herein report that rhodium-catalyzed addition reactions of sodium tetraarylborates to acylsilanes yield distinct arylation products depending on the reaction conditions employed.

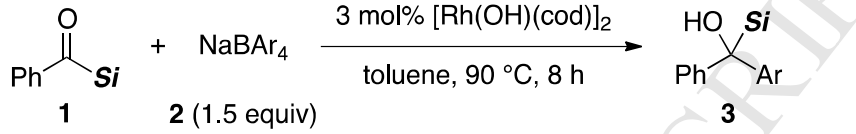
2. Results and discussion

We began our investigation with the rhodium-catalyzed arylation of benzoyltrimethylsilane (**1a**). When benzoylsilane **1a** was reacted with sodium tetraphenylborate (**2a**) in toluene at 90 °C in the presence of a catalytic amount of $[Rh(OH)(cod)]_2$ (cod = cycloocta-1,5-diene), 1,2-addition of arylrhodium(I) species to the carbonyl group of **1a** occurred to give diphenyl(trimethylsilyl)methanol (**3aa**) in 68% yield (Table 1, entry 1) [8–10]. The carbonyl arylation is considered to proceed via 1,2-addition of an arylrhodium(I) species to an acylsilane C=O bond. Other tetraarylborates **2b**–**e** also participated in the reaction with **1a** to produce the corresponding α-silyl benzhydrols **3ab**–**ae** (entries 2–5). Product **3af** derived from electron-rich tetraarylborate **2af** (Ar = 4-$MeOC_6H_4$) was unstable, and it rearranged to diaryl ketone **6f** during isolation (entry 6) [11]. The half-life for the rearrangement of relatively stable **3ad** (Ar = 4-$CF_3C_6H_4$) was determined by ^{1}H NMR to be approximately two weeks at room temperature in the absence of light [12]. Benzoylsilanes bearing $SiMe_2Ph$ and $SiMe_2$*t*-Bu groups were also converted to the corresponding α-silyl benzhydrols (**3ba** and **3ca**), albeit with reduced efficacy (entries 7 and

8). In cases where $[RhCl(cod)]_2$ was used as a catalyst instead of $[Rh(OH)(cod)]_2$, a decrease in yields was observed (**3aa**: 52%, **3ba**: 44%, **3ca**: 42%).

Table 1

Rhodium-catalyzed arylation of benzoyltrimethylsilane to afford α-silyl benzhydrols **3**.[a]



Entry	**1** (***Si***)	**2** (Ar)	Product	Yield (%)
1	**1a** ($SiMe_3$)	**2a** (Ph)	**3aa**	68[b] (65)[c]
2	**1a**	**2b** (4-MeC_6H_4)	**3ab**	56
3	**1a**	**2c** (3-MeC_6H_4)	**3ac**	46
4	**1a**	**2d** (4-$CF_3C_6H_4$)	**3ad**	60
5	**1a**	**2e** (4-ClC_6H_4)	**3ae**	52
6	**1a**	**2f** (4-$MeOC_6H_4$)	**3af**	–[d]
7	**1b** ($SiMe_2Ph$)	**2a**	**3ba**	53[e]
8	**1c** ($SiMe_2t$-Bu)	**2a**	**3ca**	52[f]

[a] Conditions: **1** (0.10 mmol), **2** (0.15 mmol), and $[Rh(OH)(cod)]_2$ (3.0 μmol, 6 mol% Rh) in toluene (1.0 mL) at 90 °C for 8 h.

[b] 52% yield with $[RhCl(cod)]_2$.

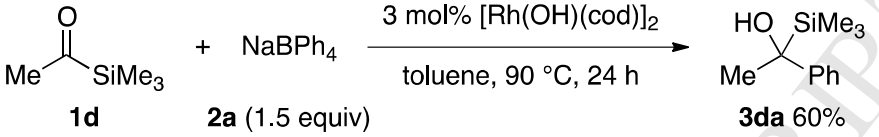
[c] Performed on a 0.5 mmol scale.

[d] Diaryl ketone **6f** was isolated in 46% yield.

[e] 44% yield with $[RhCl(cod)]_2$.

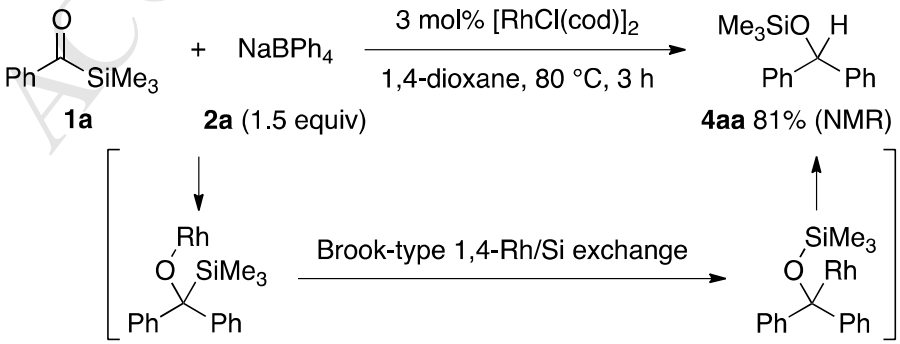
[f] 42% yield with $[RhCl(cod)]_2$.

In addition to the benzoylsilanes **1a**–**c**, acetyl(trimethylsilyl)silane (**1d**) was also utilized as the substrate for the rhodium-catalyzed arylation with **2** (Scheme 1). The reaction of **1d** and **2a** furnished 1-phenyl-1-silylethanol **3da** in 60% yield.



Scheme 1. Arylation of acetylsilane **1d** with **2a**

In contrast, the reaction performed in 1,4-dioxane in the presence of $[RhCl(cod)]_2$ provided benzhydryl trimethylsilyl ether (**4aa**) in 81% NMR yield (Scheme 2). The silyl ether **4aa** was desilylated during chromatography over silica gel to afford benzhydrol (**5a**) in 59% yield. The formation of **4aa** can be accounted for by considering the Brook-type 1,4-rhodium/silicon exchange occurring with the intermediate [diphenyl(trimethylsilyl)methoxy]rhodium(I) [13,14,15]. Similar results were obtained when the reaction was performed in the absence of light (**4aa**, 53% NMR yield), indicating that siloxycarbene generated by a photoinduced 1,2-silyl shift might not be involved in the process.

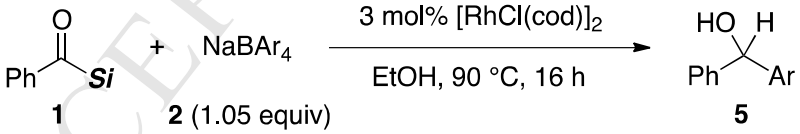


Scheme 2. Rhodium-catalyzed arylation of **1a** affording benzhydryl silyl ether **4**

The reaction performed in protic solvents led to the exclusive formation of desilylated benzhydrols **5** (Table 2). The arylation of **1a** with **2a** in EtOH in the presence of $[RhCl(cod)]_2$ produced alcohol **5a** in 73% yield. Because **3aa** was recovered unchanged when heated at 90 °C in EtOH both in the presence and absence of the rhodium catalyst, the formation of **5a** may be ascribed to the desilylation of **4aa** instead of **3aa** under these catalytic conditions. Phenyl(tolyl)methanols (**5b** and **5c**) were obtained from the reaction of **1a** with tolylborates (**2b** and **2c**) (entries 2 and 3). Although borates **2d** and **2e** failed to give benzhydrols **5**, 4-methoxyphenyl derivative **2f** was successfully arylated with **1a** to afford **5f** in 61% yield (entry 4). The use of dimethyl(phenyl)silyl derivative **1b** for the reaction with **2a** also led to the formation of desired product **5a** in 83% yield (entry 5), whereas the reaction of **1c** provided TBS ether **4ca**, which was resistant to desilylation under the investigated reaction conditions (entry 6).

Table 2

Rhodium-catalyzed arylation of **1** to afford benzhydrols **5**.[a]



Entry	**1** (***Si***)	**2** (Ar)	Product	Yield (%)
1	**1a** ($SiMe_3$)	**2a** (Ph)	**5a**	73 (84)[b]
2	**1a**	**2b** (4-MeC_6H_4)	**5b**	87
3	**1a**	**2c** (3-MeC_6H_4)	**5c**	42
4	**1a**	**2f** (4-$MeOC_6H_4$)	**5f**	61
5	**1b** ($SiMe_2Ph$)	**2a**	**5a**	83

6	**1c** ($SiMe_2t$-Bu)	**2a**[c]	**4ca**[d]	50[e]

[a] Conditions: **1** (0.10 mmol), **2** (0.15 mmol), and $[RhCl(cod)]_2$ (3.0 μmol, 6 mol% Rh) in EtOH (1.0 mL) at 90 °C for 16 h.

[b] Performed on a 0.5 mmol scale (14 h).

[c] 1.5 equiv of **2a** was used.

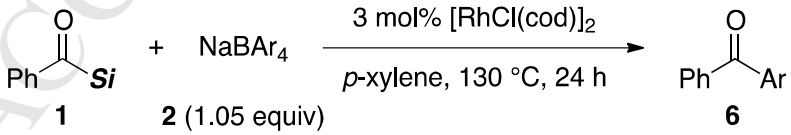
[d] Benzhydryl *tert*-butyldimethylsilyl ether.

[e] 69% yield with 3 equiv of **2a**.

The rhodium-catalyzed arylation of **1** under more forcing conditions gave rise to diaryl ketones **6** (Table 3) [16,17]. Because the oxidation of alcohols **5** to ketone **6** under the investigated reaction conditions was virtually unnoticeable, **6** appears to be formed directly from α-silyl benzhydrols **3**. Indeed, heating **3aa** at 130 °C in *p*-xylene for 24 h, irrespective of the presence of the rhodium catalyst, resulted in the formation of **6a** (49% yield without Rh; 28% yield with Rh), in contrast to the inertness of **3** in solution at temperatures less than 90 °C (*vide supra*).

Table 3

Rhodium-catalyzed arylation of **1** to afford diaryl ketones **6**.[a]



Entry	**1** (***Si***)	**2** (Ar)	Product	Yield (%)
1	**1a** ($SiMe_3$)	**2a** (Ph)	**6a**	67 (73)[b]
2	**1a**	**2b** (4-MeC_6H_4)	**6b**	47
3	**1a**	**2c** (3-MeC_6H_4)	**6c**	55[c]

4	**1a**	**2d** (4-$CF_3C_6H_4$)	**6d**	53
5	**1a**	**2e** (4-ClC_6H_4)	**6e**	40
6	**1a**	**2f** (4-$MeOC_6H_4$)	**6f**	39[c]
7	**1b** ($SiMe_2Ph$)	**2a**[d]	**6a**	68
8	**1c** ($SiMe_2t$-Bu)	**2a**[d]	**6a**	36[e]

[a] Conditions: **1** (0.10 mmol), **2** (0.15 mmol), and $[RhCl(cod)]_2$ (3.0 μmol, 6 mol% Rh) in *p*-xylene (1.0 mL) at 130 °C for 24 h.

[b] Performed on a 0.5 mmol scale (45 h).

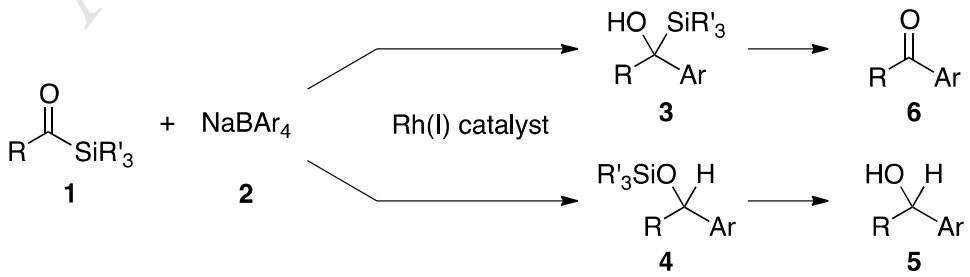
[c] Determined by ^1H NMR.

[d] 1.5 equiv of **2a** was used.

[e] 46% yield with 3.0 equiv of **2a**.

3. Conclusion

In summary, the addition of sodium tetraarylborates **2** to acylsilanes **1** occurred in the presence of rhodium(I) catalysts. The reaction gave α-silyl benzhydrols **3**, benzhydryl silyl ethers **4**, benzhydrols **5**, and diaryl ketones **6** depending on the conditions employed (Scheme 3). Alcohols **5** and ketones **6** were derived only from silyl ethers **4** and silyl alcohols **3**, respectively.



Scheme 3. Diagram for the rhodium-catalyzed arylation of acylsilanes

4. Experimental section

4.1 General Procedure for the rhodium-catalyzed arylation of acylsilanes with sodium tetraarylborates

A Schlenk tube was charged with sodium tetraarylborate **2** (0.150 mmol) and $[Rh(OH)(cod)]_2$ (3 μmol, 6 mol% Rh). The tube was evacuated and backfilled with nitrogen, and then acylsilane **1** (0.100 mmol) and toluene (1.0 mL) were added via syringe through the septum. After being heated at 90 °C for 8 h, the reaction mixture was filtered through a plug of Florisil® washing with hexane–AcOEt (5:1), and the filtrate was concentrated. Purification by preparative TLC on silica gel (hexane–AcOEt) afforded α-silyl benzhydrol **3**.

*4.1.1. Diphenyl(trimethylsilyl)methanol (**3aa**).*

Pale yellow oil. IR (ν/cm^{-1}): 2962, 1250, 837, 760, 702; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.13 (s, 9H), 1.97 (s, 1H), 7.17–7.24 (m, 2H), 7.27–7.38 (m, 8H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ –2.3, 75.7, 126.2, 126.6, 128.0, 146.6; HRMS (ESI) calcd for $C_{16}H_{20}NaOSi$ $[M + Na]^+$ 279.1176, found 279.1179.

*4.1.2. Phenyl(p-tolyl)(trimethylsilyl)methanol (**3ab**).*

Pale yellow oil. IR (ν/cm^{-1}): 3487, 2962, 1651, 1281, 1250, 841, 702; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.13 (s, 9H), 1.93 (s, 1H), 2.33 (s, 3H), 7.12 (d, J = 8.4 Hz, 2H), 7.15–7.36

(m, 7H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ –2.3, 75.5, 126.0, 126.4, 126.7, 127.9, 128.8, 135.8, 143.8, 146.8; HRMS (ESI) calcd for $C_{17}H_{22}NaOSi$ $[M + Na]^+$ 293.1332, found 293.1327.

*4.1.3. Phenyl(m-tolyl)(trimethylsilyl)methanol (**3ac**).*

Pale yellow oil. IR (ν/cm^{-1}): 2962, 1250, 841, 748, 702; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.13 (s, 9H), 1.96 (s, 1H), 2.33 (s, 3H), 7.02 (d, J = 7.5 Hz, 1H), 7.15–7.24 (m, 4H), 7.27–7.37 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ –2.3, 21.7, 75.6, 123.8, 126.1, 126.5, 127.0, 127.2, 127.8, 128.0, 137.7, 146.6, 146.7; HRMS (ESI) calcd for $C_{17}H_{22}NaOSi$ $[M + Na]^+$ 293.1332, found 293.1331.

*4.1.4. Phenyl[4-(trifluoromethyl)phenyl](trimethylsilyl)methanol (**3ad**).*

Pale yellow oil. IR (ν/cm^{-1}): 3479, 2962, 1250, 1103, 887, 841, 756, 702; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 9H), 1.93 (s, 1H), 7.15–7.38 (m, 7H), 7.42–7.52 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ –2.4, 75.7, 124.3 (q, $^1J_{C–F}$ = 271.5 Hz), 124.8 (q, $^3J_{C–F}$ = 3.7 Hz), 125.7, 126.4, 126.9, 128.0 (q, $^2J_{C–F}$ = 32.3 Hz), 128.4, 146.1, 150.5; HRMS (ESI) calcd for $C_{17}H_{19}F_3NaOSi$ $[M + Na]^+$ 347.1049, found 347.1055.

*4.1.5. (4-Chlorophenyl)(phenyl)(trimethylsilyl)methanol (**3ae**).*

Pale yellow oil. IR (ν/cm^{-1}): 3479, 2962, 1250, 1211, 1095, 1003, 887, 841, 764; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.12 (s, 9H), 1.96 (br s, 1H), 7.19–7.35 (m, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ –2.4, 75.3, 126.6, 126.7, 127.8, 128.0, 128.2, 131.8, 145.1, 146.3; HRMS (ESI) calcd for $C_{16}H_{19}ClNaOSi$ $[M + Na]^+$ 313.0786, found 313.0792.

*4.1.6. [Dimethyl(phenyl)silyl]diphenylmethanol (**3ba**).*

Pale yellow oil. IR (ν/cm^{-1}): 3556, 3062, 1250, 810, 741, 702; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.39 (s, 6H), 2.08 (s, 1H), 7.15–7.41 (m, 15H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ –3.9, 75.7, 126.2, 126.6, 127.6, 127.9, 129.3, 135.0, 136.4, 146.0; HRMS (ESI) calcd for $C_{21}H_{22}NaOSi$ $[M + Na]^+$ 341.1332, found 341.1332.

*4.1.7. (tert-Butyldimethylsilyl)diphenylmethanol (**3ca**).*

Pale yellow oil. IR (ν/cm^{-1}): 3444, 2958, 1246, 841, 760, 702; ^{1}H NMR (300 MHz, $CDCl_3$) δ –0.01 (s, 9H), 1.46 (br s, 1H), 1.63 (s, 3H), 7.14–7.21 (m, 1H), 7.28–7.36 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ –4.3, 25.9, 69.8, 124.4, 125.3, 127.9, 148.1; HRMS (ESI) calcd for $C_{11}H_{18}NaOSi$ $[M + Na]^+$ 217.1019, found 217.1020.

*4.1.8. 1-Phenyl-1-(trimethylsilyl)ethanol (**3da**).*

Pale yellow oil. IR (ν/cm^{-1}): 3444, 2958, 1246, 841, 760, 702; ^{1}H NMR (300 MHz, $CDCl_3$) δ –0.01 (s, 9H), 1.46 (br s, 1H), 1.63 (s, 3H), 7.14–7.21 (m, 1H), 7.28–7.36 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ –4.3, 25.9, 69.8, 124.4, 125.3, 127.9, 148.1; HRMS (ESI) calcd for $C_{11}H_{18}NaOSi$ $[M + Na]^+$ 217.1019, found 217.1020.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.XXXX.XX.XXX.

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(b) K. Oguma, M. Miura, T. Satoh, M. Nomura, J. Organomet. Chem. 648 (2002) 297–301;

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[9] All reactions in this study were performed under room fluorescent lighting.

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[12] At 0 °C, **3ad** remained largely unchanged after one month.

[13] We thank one of the reviewers for suggesting this mechanism.

[14] Treatment of **3aa** with KOH in 1,4-dioxane–H_2O (100:1) at 80 °C resulted in a clean conversion to **5a**. However, **3aa** remained unaltered when heated at 80 °C in 1,4-dioxane, both in the presence and absence of the rhodium catalyst.

[15] Brook-type Si–C–O–Cu → Cu–C–O–Si rearrangement was investigated in detail. See ref 10a.

[16] For rhodium-catalyzed synthesis of ketones from aldehydes and potassium aryltrifluoroborates under hydrogen transfer conditions, see O. Chuzel, A. Roesch, J.-P. Genet, S. Darses, J. Org. Chem. 73 (2008) 7800–7802. See also ref 2g.

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• Addition of sodium tetraarylborates to acylsilanes occurs in the presence of rhodium(I) catalysts.

• Four different arylated products are obtained depending on the reaction conditions employed.

• α-Silyl benzhydrols are converted into the corresponding dirayl ketones.

Supporting Information

Rhodium-catalyzed arylation of acylsilanes with sodium tetraarylborates

Takanori Matsuda *, Kohei Mizuno, Shoichi Watanuki

Department of Applied Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

E-mail: mtd@rs.tus.ac.jp

General. All reactions were carried out with standard Schlenk techniques. Column chromatography was carried out on Wakogel C-200 (75–150 μm). Preparative thin-layer chromatography was performed on Wakogel® B-5F. Proton chemical shifts were referenced to residual $CHCl_3$ signal at 7.26 ppm. Carbon chemical shifts were referenced to $CDCl_3$ at 77.0 ppm.

Materials. Acylsilanes (**1b** and **1c**) [1] and sodium tetraarylborates (**2b**–**f**) [2] were prepared by the literature methods. All other commercially available chemical resources were used as received without further purification.

[1] J.R. Huckins, S.D. Rychnovsky, J. Org. Chem. 68 (2003) 10135–10145.

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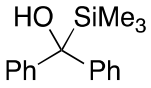
(b) R. Shintani, Y. Tsutsumi, M. Nagaosa, T. Nishimura, T. Hayashi, J. Am. Chem. Soc. 131 (2009) 13588–13589.

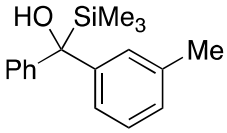
General Procedure: Rhodium-Catalyzed Arylation of Acylsilanes 1 with Sodium Tetraarylborates 2



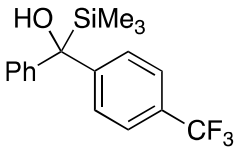
Diphenyl(trimethylsilyl)methanol (3aa). Table 1, Entry 1: A Schlenk tube was charged with $NaBPh_4$ (**2a**, 51.5 mg, 0.150 mmol) and $[Rh(OH)(cod)]_2$ (1.4 mg, 3.1 μmol, 6 mol% Rh). The tube was evacuated and backfilled with nitrogen, and then benzoyltrimethylsilane (**1a**, 17.9 mg, 0.100 mmol) and toluene (1.0 mL) were added via syringe through the septum. The mixture was heated at 90 °C for 8 h. The reaction mixture was filtered through a plug of Florisil® washing with hexane–AcOEt (5:1), and the filtrate was concentrated. Purification by preparative TLC on silica gel (hexane:AcOEt = 8:1) afforded the title compound (**3aa**, 17.6 mg, 0.069 mmol, 68%) as a pale yellow oil. IR (ν/cm^{-1}): 2962, 1250, 837, 760, 702; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.13 (s, 9H), 1.97 (s, 1H), 7.17–7.24 (m, 2H), 7.27–7.38 (m, 8H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ –2.3, 75.7, 126.2, 126.6, 128.0, 146.6; HRMS (ESI) calcd for $C_{16}H_{20}NaOSi$ $[M + Na]^+$ 279.1176, found 279.1179.

Phenyl(*p*-tolyl)(trimethylsilyl)methanol (3ab). Table 1, Entry 2: According to the General Procedure, **1a** (17.1 mg, 0.096 mmol), **2b** (60.0 mg, 0.151 mmol), and $[Rh(OH)(cod)]_2$ (1.5 mg, 3.3 μmol, 7 mol% Rh) were reacted in toluene (1.0 mL) at 90 °C for 6.5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 15:1) afforded the title compound (14.6 mg, 0.054 mmol, 56%) as a pale yellow oil. IR (ν/cm^{-1}): 3487, 2962, 1651, 1281, 1250, 841, 702; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.13 (s, 9H), 1.93 (s, 1H), 2.33 (s, 3H), 7.12 (d, J = 8.4 Hz, 2H), 7.15–7.36 (m, 7H); ^{13}C

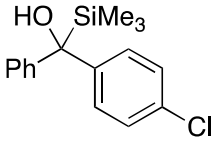
NMR (75.5 MHz, $CDCl_3$) δ –2.3, 75.5, 126.0, 126.4, 126.7, 127.9, 128.8, 135.8, 143.8, 146.8; HRMS (ESI) calcd for $C_{17}H_{22}NaOSi$ $[M + Na]^+$ 293.1332, found 293.1327.



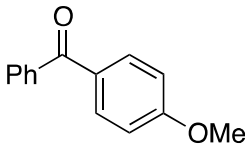
Phenyl(*m*-tolyl)(trimethylsilyl)methanol (3ac). Table 1, Entry 3: According to the General Procedure, **1a** (17.3 mg, 0.097 mmol), **2c** (59.6 mg, 0.150 mmol), and $[Rh(OH)(cod)]_2$ (1.5 mg, 3.3 μmol, 7 mol% Rh) were reacted in toluene (1.0 mL) at 90 °C for 2.5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 20:1) afforded the title compound (12.2 mg, 0.045 mmol, 46%) as a pale yellow oil. IR (ν/cm^{-1}): 2962, 1250, 841, 748, 702; ^1H NMR (300 MHz, $CDCl_3$) δ 0.13 (s, 9H), 1.96 (s, 1H), 2.33 (s, 3H), 7.02 (d, J = 7.5 Hz, 1H), 7.15–7.24 (m, 4H), 7.27–7.37 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ –2.3, 21.7, 75.6, 123.8, 126.1, 126.5, 127.0, 127.2, 127.8, 128.0, 137.7, 146.6, 146.7; HRMS (ESI) calcd for $C_{17}H_{22}NaOSi$ $[M + Na]^+$ 293.1332, found 293.1331.



Phenyl[4-(trifluoromethyl)phenyl](trimethylsilyl)methanol (3ad). Table 1, Entry 4: According to the General Procedure, **1a** (16.1 mg, 0.090 mmol), **2d** (92.1 mg, 0.150 mmol), and $[Rh(OH)(cod)]_2$ (1.4 mg, 3.1 μmol, 7 mol% Rh) were reacted in toluene (1.0 mL) at 100 °C for 2.5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 20:1) afforded the title compound (17.5 mg, 0.054 mmol, 60%) as a pale yellow oil. IR (ν/cm^{-1}): 3479, 2962, 1250, 1103, 887, 841, 756, 702; ^1H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 9H), 1.93 (s, 1H), 7.15–7.38 (m, 7H), 7.42–7.52 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ –2.4, 75.7, 124.3 (q, $^1J_{C–F}$ = 271.5 Hz), 124.8 (q, $^3J_{C–F}$ = 3.7 Hz), 125.7, 126.4, 126.9, 128.0 (q, $^2J_{C–F}$ = 32.3 Hz), 128.4, 146.1, 150.5; HRMS (ESI) calcd for $C_{17}H_{19}F_3NaOSi$ $[M + Na]^+$ 347.1049, found 347.1055.



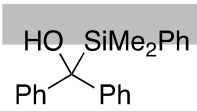
(4-Chlorophenyl)(phenyl)(trimethylsilyl)methanol (3ae). Table 1, Entry 5: According to the General Procedure, **1a** (17.9 mg, 0.100 mmol), **2e** (72.0 mg, 0.150 mmol), and $[Rh(OH)(cod)]_2$ (1.4 mg, 3.1 µmol, 6 mol% Rh) were reacted in toluene (1.0 mL) at 90 °C for 2 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 20:1) afforded the title compound (15.1 mg, 0.052 mmol, 52%) as a pale yellow oil. IR (ν/cm^{-1}): 3479, 2962, 1250, 1211, 1095, 1003, 887, 841, 764; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.12 (s, 9H), 1.96 (br s, 1H), 7.19–7.35 (m, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ –2.4, 75.3, 126.6, 126.7, 127.8, 128.0, 128.2, 131.8, 145.1, 146.3; HRMS (ESI) calcd for $C_{16}H_{19}ClNaOSi$ $[M + Na]^+$ 313.0786, found 313.0792.



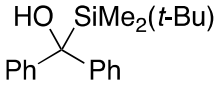
(4-Methoxyphenyl)(phenyl)methanone (6f). Table 1, Entry 6: According to the General Procedure, **1a** (17.8 mg, 0.100 mmol), **2f** (69.3 mg, 0.150 mmol), and $[Rh(OH)(cod)]_2$ (1.4 mg, 6.4 µmol, 6 mol% Rh) were reacted in toluene (1.0 mL) at 90 °C for 18 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 8:1) afforded the title compound (9.8 mg, 0.046 mmol, 46%) as white solid. ^{1}H and ^{13}C NMR spectra were identical to those in the literature [3].

Table 3, Entry 6: 1a (17.0 mg, 0.095 mmol), **2f** (46.7 mg, 0.101 mmol), and $[RhCl(cod)]_2$ (1.6 mg, 3.2 µmol, 7 mol% Rh) were reacted in *p*-xylene (1.0 mL) at 130 °C for 42 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 15:1) afforded an inseparable mixture of **6f** and 4,4′-dimethoxy-1,1′-biphenyl (10.7 mg, 75:25 by ^{1}H NMR, 39%).

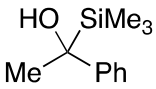
[3] D. Xing, B. Guan, G. Cai, Z. Fang, L. Yang, Z. Shi, Org. Lett. 8 (2006) 693–696.



[Dimethyl(phenyl)silyl]diphenylmethanol (3ba). Table 1, Entry 7: According to the General Procedure, **1b** (24.0 mg, 0.100 mmol), **2a** (51.4 mg, 0.150 mmol), and $[Rh(OH)(cod)]_2$ (1.4 mg, 3.1 μmol, 6 mol% Rh) were reacted in toluene (1.0 mL) at 90 °C for 6 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 15:1) afforded the title compound (16.9 mg, 0.053 mmol, 53%) as a pale yellow oil. IR (ν/cm^{-1}): 3556, 3062, 1250, 810, 741, 702; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.39 (s, 6H), 2.08 (s, 1H), 7.15–7.41 (m, 15H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ –3.9, 75.7, 126.2, 126.6, 127.6, 127.9, 129.3, 135.0, 136.4, 146.0; HRMS (ESI) calcd for $C_{21}H_{22}NaOSi$ $[M + Na]^+$ 341.1332, found 341.1332.

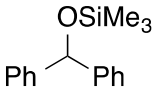


(*tert*-Butyldimethylsilyl)diphenylmethanol (3ca). Table 1, Entry 8: According to the General Procedure, **1c** (22.0 mg, 0.100 mmol), **2a** (51.4 mg, 0.150 mmol), and $[Rh(OH)(cod)]_2$ (1.4 mg, 3.1 μmol, 6 mol% Rh) were reacted in toluene (1.0 mL) at 90 °C for 10 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 20:1) afforded the title compound (15.5 mg, 0.052 mmol, 52%) as a pale yellow oil. IR (ν/cm^{-1}): 3518, 2931, 2854, 1257, 833, 764, 702; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 6H), 0.77 (s, 9H), 2.01 (s, 1H), 7.15–7.23 (m, 2H), 7.26–7.35 (m, 4H), 7.44–7.52 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ –5.2, 18.8, 28.1, 76.9, 126.0, 126.1, 127.9, 146.8; HRMS (ESI) calcd for $C_{19}H_{26}NaOSi$ $[M + Na]^+$ 321.1645, found 321.1641.

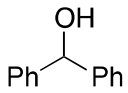


1-Phenyl-1-(trimethylsilyl)ethanol (3da). Scheme 1: According to the General Procedure, **1d** (11.8 mg, 0.102 mmol), **2a** (51.4 mg, 0.150 mmol), and $[Rh(OH)(cod)]_2$ (1.4 mg, 3.1 μmol, 6 mol% Rh) were reacted in toluene (1.0 mL) at 90 °C for 12 h. Purification by preparative TLC on

silica gel (hexane:AcOEt = 10:1) afforded the title compound (11.8 mg, 0.061 mmol, 60%) as a pale yellow oil. IR (ν/cm^{-1}): 3444, 2958, 1246, 841, 760, 702; ^{1}H NMR (300 MHz, $CDCl_3$) δ –0.01 (s, 9H), 1.46 (br s, 1H), 1.63 (s, 3H), 7.14–7.21 (m, 1H), 7.28–7.36 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ –4.3, 25.9, 69.8, 124.4, 125.3, 127.9, 148.1; HRMS (ESI) calcd for $C_{11}H_{18}NaOSi$ [M + Na]$^+$ 217.1019, found 217.1020.



(Benzhydryloxy)trimethylsilane (4aa). Scheme 2: According to the General Procedure, **1a** (17.9 mg, 0.100 mmol), **2a** (51.4 mg, 0.150 mmol), and $[RhCl(cod)]_2$ (1.5 mg, 3.0 µmol, 6 mol% Rh) were reacted in 1,4-dioxane (1.0 mL) at 80 °C for 2 h. Purification by preparative TLC on silica gel (neutral, hexane:AcOEt = 10:1) afforded an inseparable mixture of **4aa** and biphenyl (23.1 mg, 85:15 by ^{1}H NMR, 81%). ^{1}H and ^{13}C NMR spectra were identical to those in the literature [4].

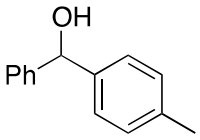


Diphenylmethanol (5a). Table 2, Entry 1: According to the General Procedure, **1a** (24.8 mg, 0.139 mmol), **2a** (52.3 mg, 0.153 mmol), and $[RhCl(cod)]_2$ (2.2 mg, 4.5 µmol, 6 mol% Rh) were reacted in EtOH (1.5 mL) at 90 °C for 13.5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 8:1) afforded the title compound (18.6 mg, 0.101 mmol, 73%) as a white solid. Mp. 65–66 °C. ^{1}H and ^{13}C NMR spectra were identical to those in the literature [5].

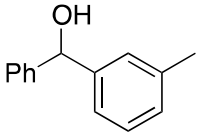
Table 2, Entry 5: 1b (24.0 mg, 0.10 mmol), **2a** (35.9 mg, 0.105 mmol), and $[RhCl(cod)]_2$ (1.5 mg, 3.0 µmol, 6 mol% Rh) were reacted in EtOH (1.0 mL) at 80 °C for 4 h. Purification by

[4] G. Rajagopal, H. Lee, S.S. Kim, Tetrahedron 65 (2009) 4735–4741.
[5] A.J. Ruddy, C.M. Kelly, S.M. Crawford, C.A. Wheaton, O.L. Sydora, B.L. Small, M. Stradiotto, L. Turculet, Organometallics 32 (2013) 5581–5588.

preparative TLC on silica gel (hexane:AcOEt = 15:1) afforded the title compound (15.3 mg, 0.083 mmol, 83%) as a white solid.

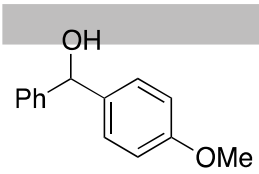


Phenyl(*p*-tolyl)methanol (5b). Table 2, Entry 2: According to the General Procedure, **1a** (16.4 mg, 0.092 mmol), **2b** (39.7 mg, 0.100 mmol), and $[RhCl(cod)]_2$ (1.4 mg, 2.8 µmol, 6 mol% Rh) were reacted in EtOH (1.0 mL) at 80 °C for 5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) afforded the title compound (15.8 mg, 0.080 mmol, 87%) as a white solid. Mp. 53–54 °C. ^{1}H and ^{13}C NMR spectra were identical to those in the literature [6].

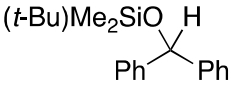


Phenyl(*m*-tolyl)methanol (5c). Table 2, Entry 3: According to the General Procedure, **1a** (17.5 mg, 0.098 mmol), **2c** (39.8 mg, 0.100 mmol), and $[RhCl(cod)]_2$ (1.5 mg, 3.0 µmol, 6 mol% Rh) were reacted in EtOH (1.0 mL) at 90 °C for 4 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 8:1) afforded the title compound (8.1 mg, 0.041 mmol, 42%) as a white solid. Mp. 52.5–53.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.34 (s, 3H), 5.82 (s, 1H), 7.06–7.11 (m, 1H), 7.14–7.42 (m, 8H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 21.5, 76.3, 123.6, 126.5, 127.2, 127.5, 128.3, 128.4, 128.5, 138.2, 143.7, 143.8; HRMS (ESI) calcd for $C_{14}H_{14}NaO$ $[M + Na]^+$ 221.0937, found 221.0938.

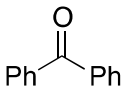
[6] A.A. Oluyadi, S. Ma, S.; C.N. Muhoro, Organometallics 32 (2013) 70–78.



(4-Methoxyphenyl)(phenyl)methanol (5f). Table 2, Entry 4: According to the General Procedure, **1a** (17.8 mg, 0.100 mmol), **2f** (48.5 mg, 0.105 mmol), and $[RhCl(cod)]_2$ (1.5 mg, 3.0 µmol, 6 mol% Rh) were reacted in EtOH (1.0 mL) at 80 °C for 12 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 10:1) afforded the title compound (13.1 mg, 0.061 mmol, 61%) as a white solid. Mp 63–64 °C. ^{1}H and ^{13}C NMR spectra were identical to those in the literature [7].



(Benzhydryloxy)(*tert*-butyl)dimethylsilane (4ca). Table 2, Entry 6: According to the General Procedure, **1c** (22.0 mg, 0.100 mmol), **2a** (51.4 mg, 0.150 mmol), and $[RhCl(cod)]_2$ (1.5 mg, 3.0 µmol, 6 mol% Rh) were reacted in EtOH (1.0 mL) at 80 °C for 4 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 20:1) afforded the title compound (15.0 mg, 0.050 mmol, 50%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ –0.05 (s, 6H), 0.90 (s, 9H), 5.73 (s, 1H), 7.14–7.21 (m, 2H), 7.22–7.29 (m, 4H), 7.30–7.36 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ –4.9, 18.3, 25.8, 76.6, 126.3, 126.9, 128.1, 145.2; HRMS (ESI) calcd for $C_{19}H_{26}NaOSi$ $[M + Na]^+$ 321.1645, found 321.1644.



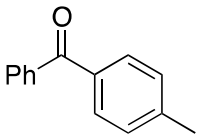
Benzophenone (6a). Table 3, Entry 1: According to the General Procedure, **1a** (17.8 mg, 0.100 mmol), **2a** (35.9 mg, 0.105 mmol), and $[RhCl(cod)]_2$ (1.5 mg, 3.0 µmol, 6 mol% Rh) were reacted in *p*-xylene (1.0 mL) at 130 °C for 24 h. Purification by preparative TLC on silica gel

[7] M. Kuriyama, N. Ishiyama, R. Shimazawa, O. Onomura, Tetrahedron 66 (2010) 6814–6819.

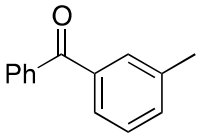
(hexane:AcOEt = 20:1) afforded the title compound (12.2 mg, 0.067 mmol, 67%) as a white solid. Mp. 49.0–49.5 °C. ^{1}H and ^{13}C NMR spectra were identical to those in the literature [8].

Table 3, Entry 7: 1b (24.0 mg, 0.100 mmol), **2a** (51.4 mg, 0.150 mmol), and $[RhCl(cod)]_2$ (1.5 mg, 3.0 µmol, 6 mol% Rh) were reacted in *p*-xylene (1.0 mL) at 130 °C for 24 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 20:1) afforded the title compound (12.4 mg, 0.068 mmol, 68%) as a white solid.

Table 3, Entry 8: 1c (22.0 mg, 0.100 mmol), **2a** (51.4 mg, 0.150 mmol), and $[RhCl(cod)]_2$ (1.5 mg, 3.0 µmol, 6 mol% Rh) were reacted in *p*-xylene (1.0 mL) at 130 °C for 24 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 20:1) afforded the title compound (6.6 mg, 0.036 mmol, 36%) as a white solid.



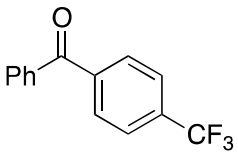
Phenyl(*p*-tolyl)methanone (6b). Table 3, Entry 2: According to the General Procedure, **1a** (26.3 mg, 0.147 mmol), **2b** (59.7 mg, 0.150 mmol), and $[RhCl(cod)]_2$ (2.3 mg, 4.7 µmol, 6 mol% Rh) were reacted in *p*-xylene (1.5 mL) at 130 °C for 42 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 15:1) afforded the title compound (13.7 mg, 0.070 mmol, 47%) as a white solid. Mp. 56.5–57.0 °C. ^{1}H and ^{13}C NMR spectra were identical to those in the literature [9].



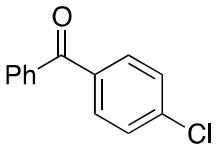
Phenyl(*m*-tolyl)methanone (6c). Table 3, Entry 3: According to the General Procedure, **1a** (17.8 mg, 0.100 mmol), **2c** (40.0 mg, 0.100 mmol), and $[RhCl(cod)]_2$ (1.5 mg, 3.0 µmol, 6 mol%

[8] L. Meng, J. Su, Z. Zha, L. Zhang, Z. Zhang, Z. Wang, Chem. Eur. J. 19 (2013) 5542–5545.
[9] W.-Y. Wu, T.-C. Lin, T. Takahashi, F.-Y. Tsai, C.-Y. Mou, ChemCatChem 5 (2013) 1011–1019.

Rh) were reacted in *p*-xylene (1.0 mL) at 130 °C for 24 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 15:1) afforded an inseparable mixture of **6c** and 3,3′-dimethyl-1,1′-biphenyl (11.4 mg, 93:7 by ^{1}H NMR, 55%). ^{1}H and ^{13}C NMR spectra were identical to those in the literature [10].



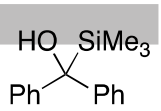
Phenyl[4-(trifluoromethyl)phenyl]methanone (6d). Table 3, Entry 4: According to the General Procedure, **1a** (16.5 mg, 0.093 mmol), **2d** (60.4 mg, 0.098 mmol), and $[RhCl(cod)]_2$ (1.4 mg, 2.8 µmol, 6 mol% Rh) were reacted in *p*-xylene (1.0 mL) at 130 °C for 36 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 15:1) afforded the title compound (12.2 mg, 0.049 mmol, 53%) as a white solid. Mp. 72–73 °C. ^{1}H and ^{13}C NMR spectra were identical to those in the literature [11].



(4-Chlorophenyl)(phenyl)methanone (6e). Table 3, Entry 5: According to the General Procedure, **1a** (17.3 mg, 0.097 mmol), **2e** (48.0 mg, 0.100 mmol), and $[RhCl(cod)]_2$ (1.5 mg, 3.0 µmol, 6 mol% Rh) were reacted in *p*-xylene (1.0 mL) at 130 °C for 30 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 8:1) afforded the title compound (8.4 mg, 0.039 mmol, 40%) as a white solid. Mp. 114–115 °C. ^{1}H and ^{13}C NMR spectra were identical to those in the literature [12].

[10] M. Li, M.; C. Wang, H. Ge, Org. Lett. 13 (2011) 2062–2064.
[11] A.T. Biju, F. Glorius, Angew. Chem., Int. Ed. 49 (2010) 9761–9764.
[12] L.J. Gooßen, F. Rudolphi, C. Oppel, N. Rodríguez, Angew. Chem., Int. Ed. 47 (2008) 3043–3045.

3aa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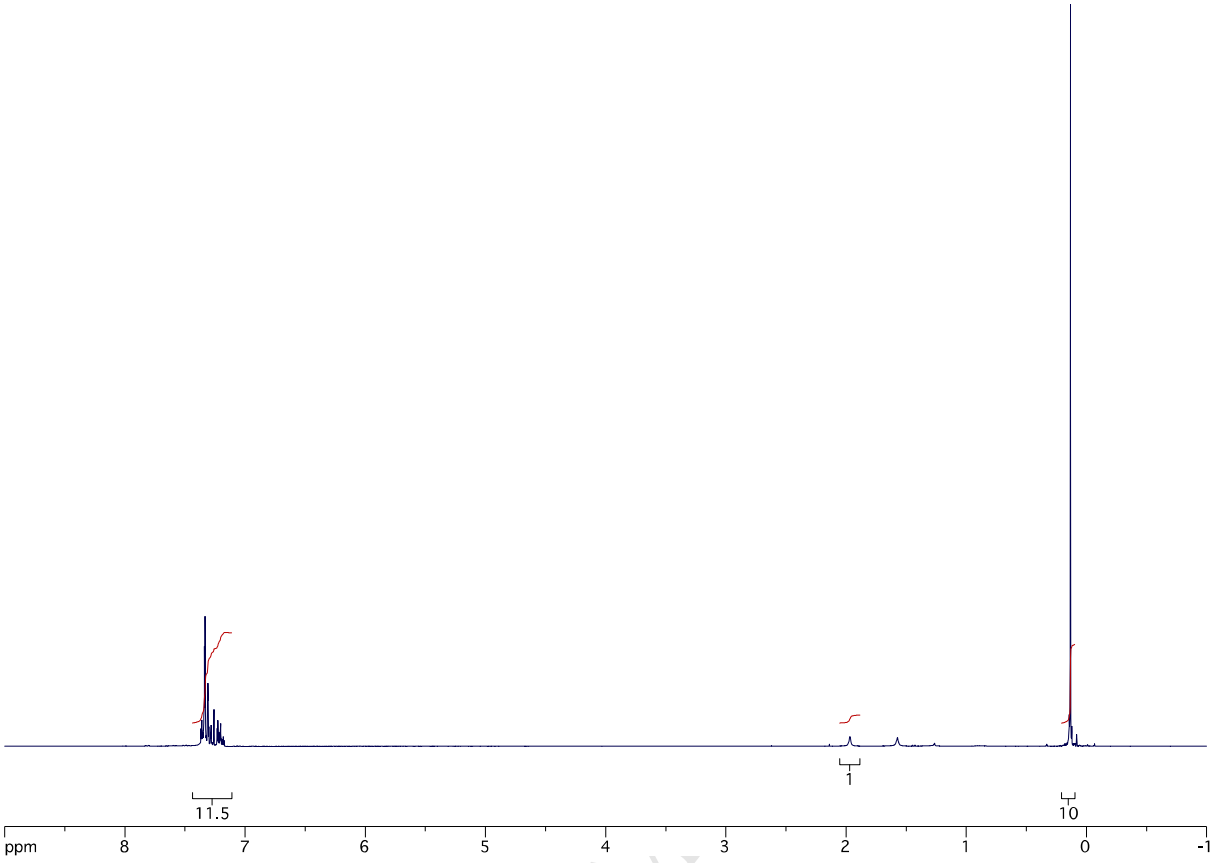
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7
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5
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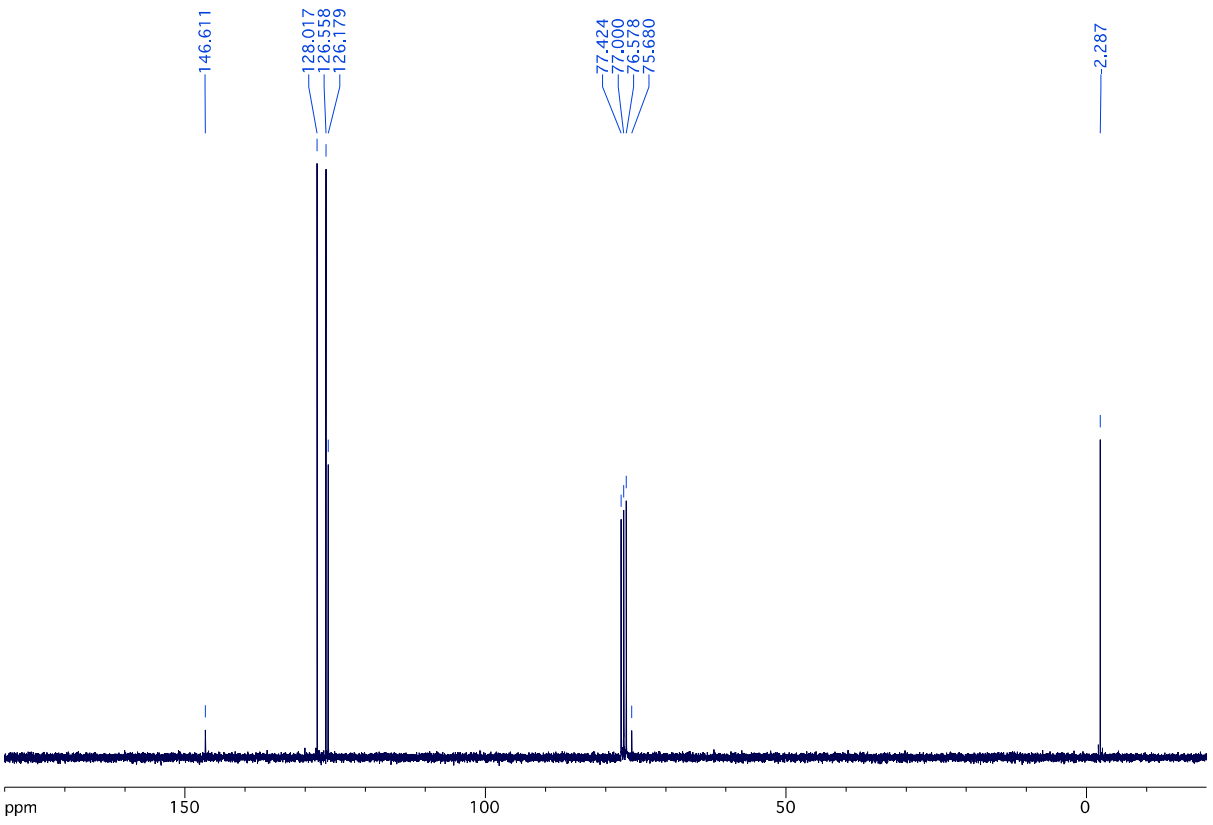
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50
0

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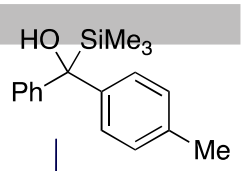
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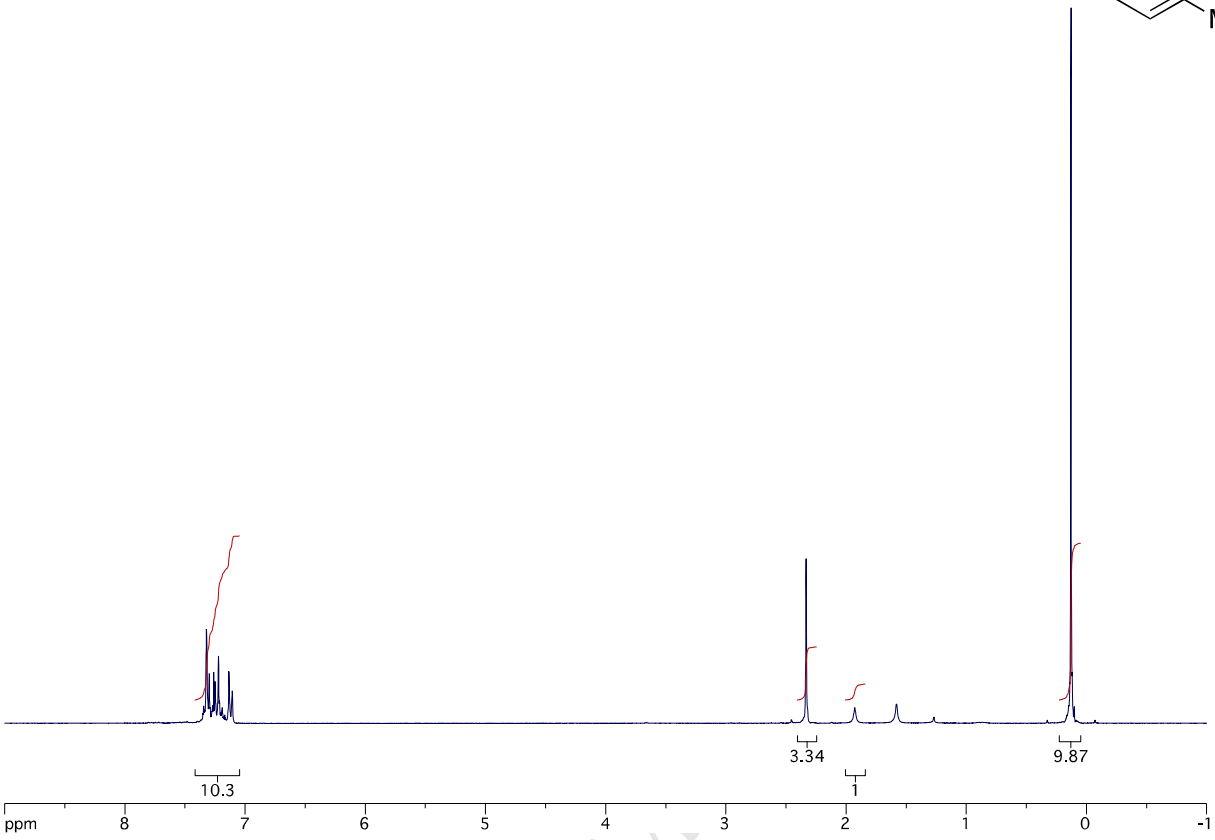
Ph
Me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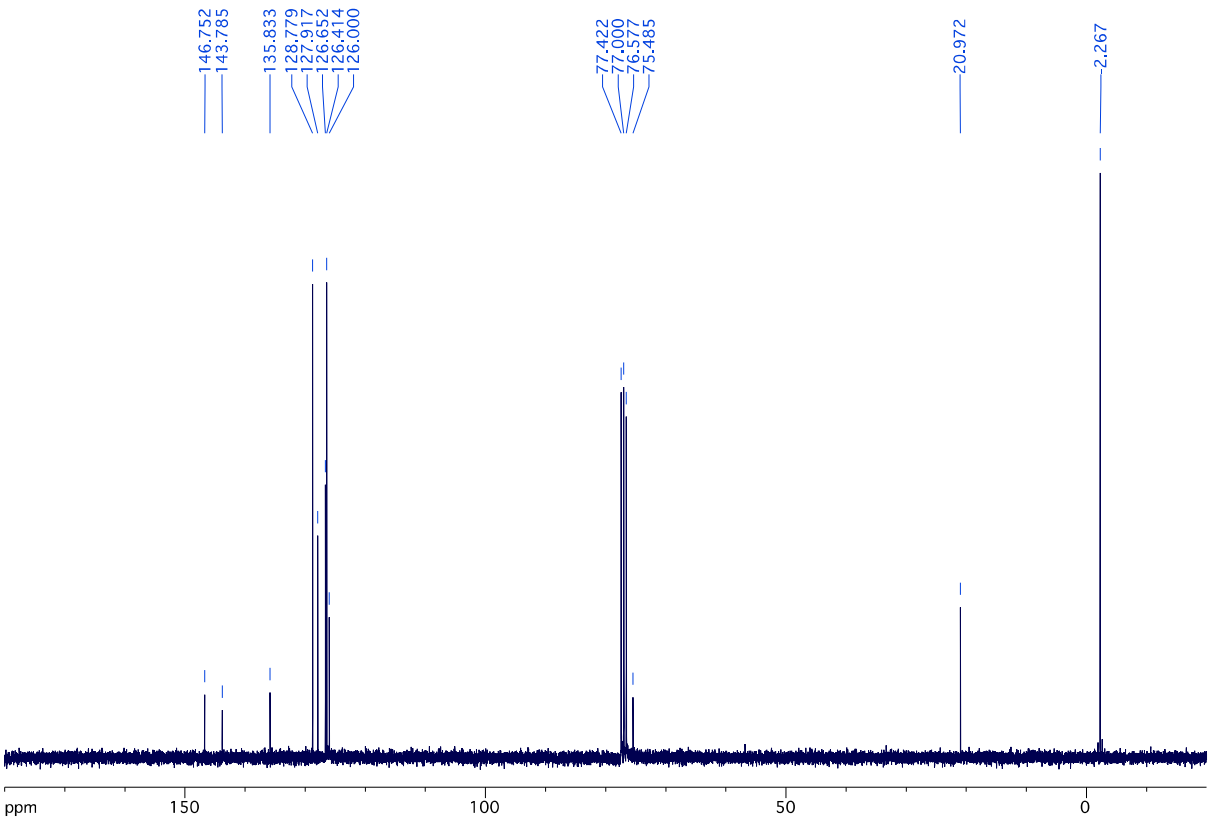
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ppm
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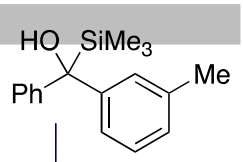
50
0

3ac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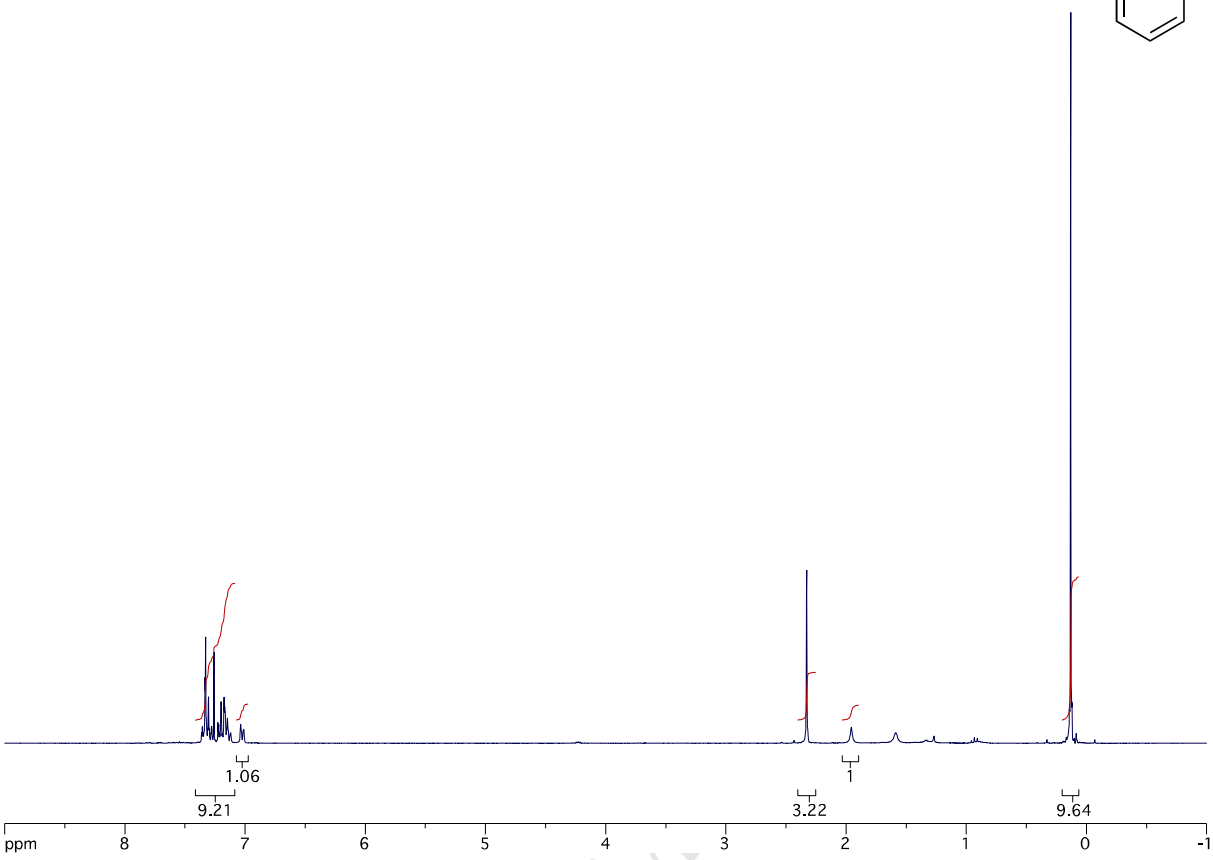
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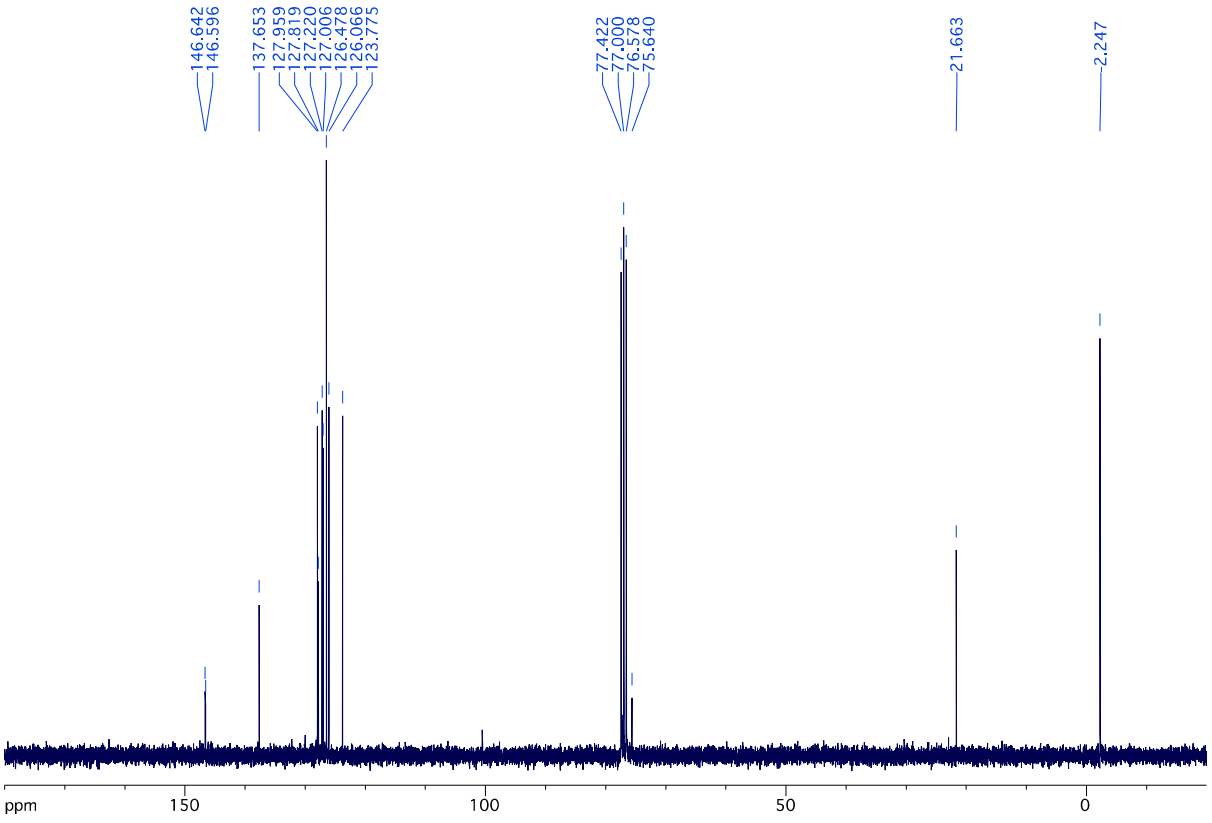
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126.478
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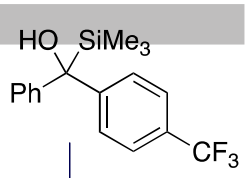
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Ph
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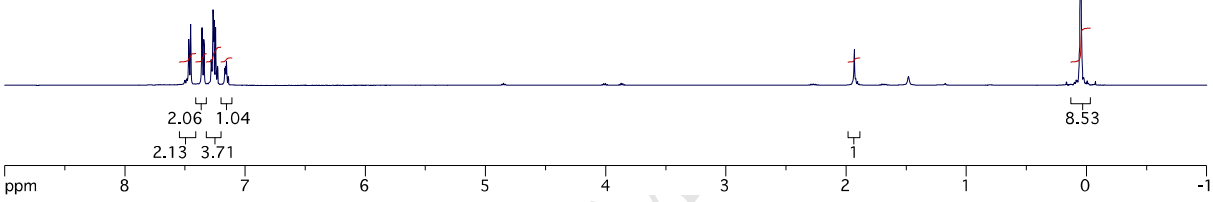
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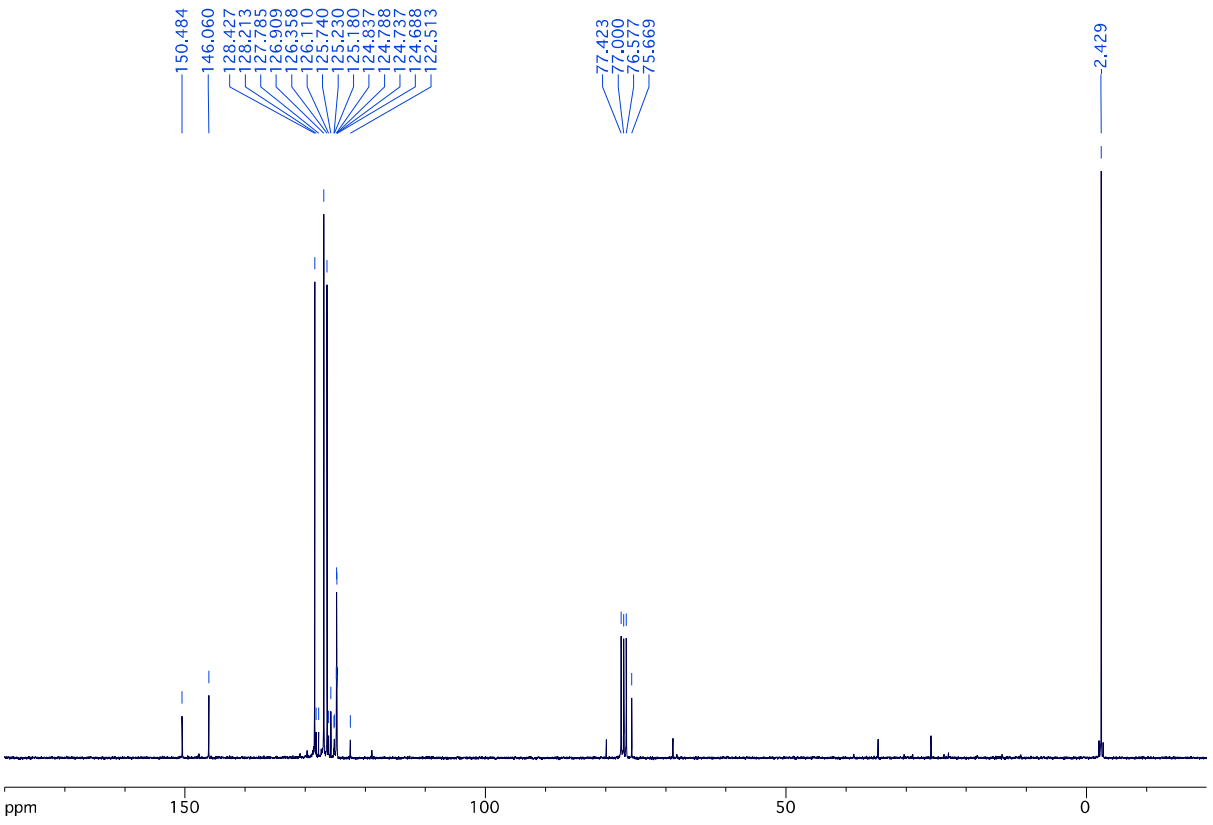
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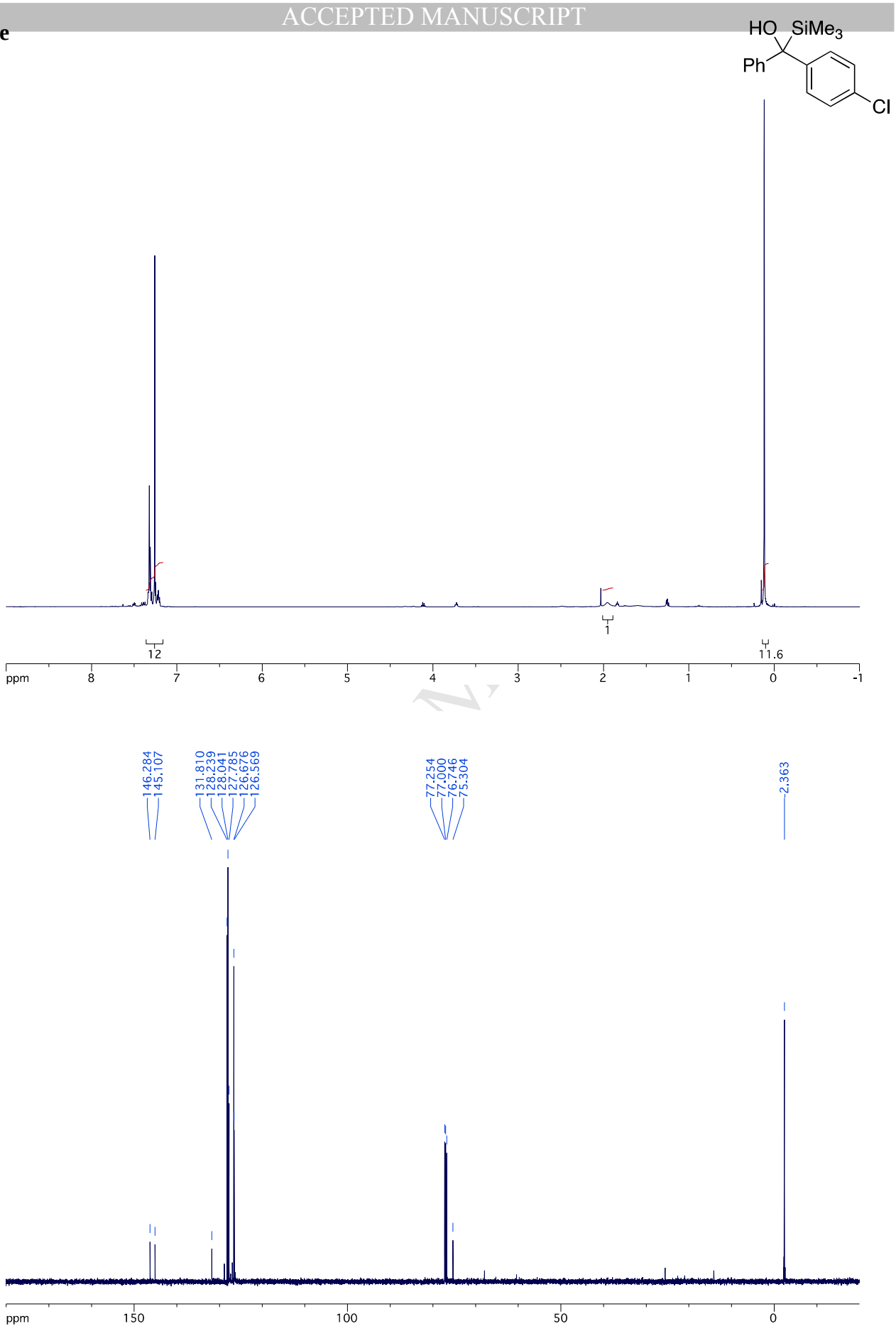
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Cl
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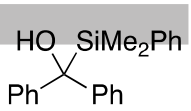
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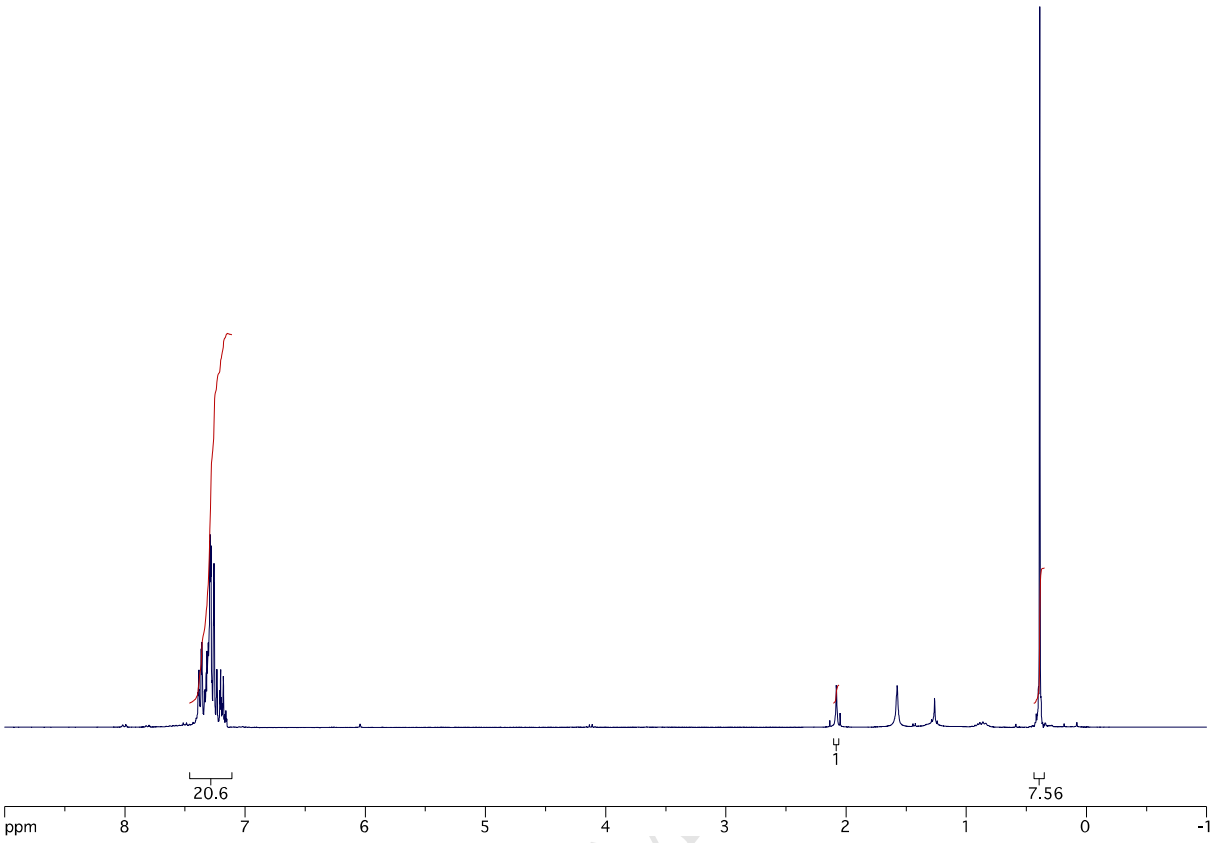
Ph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2
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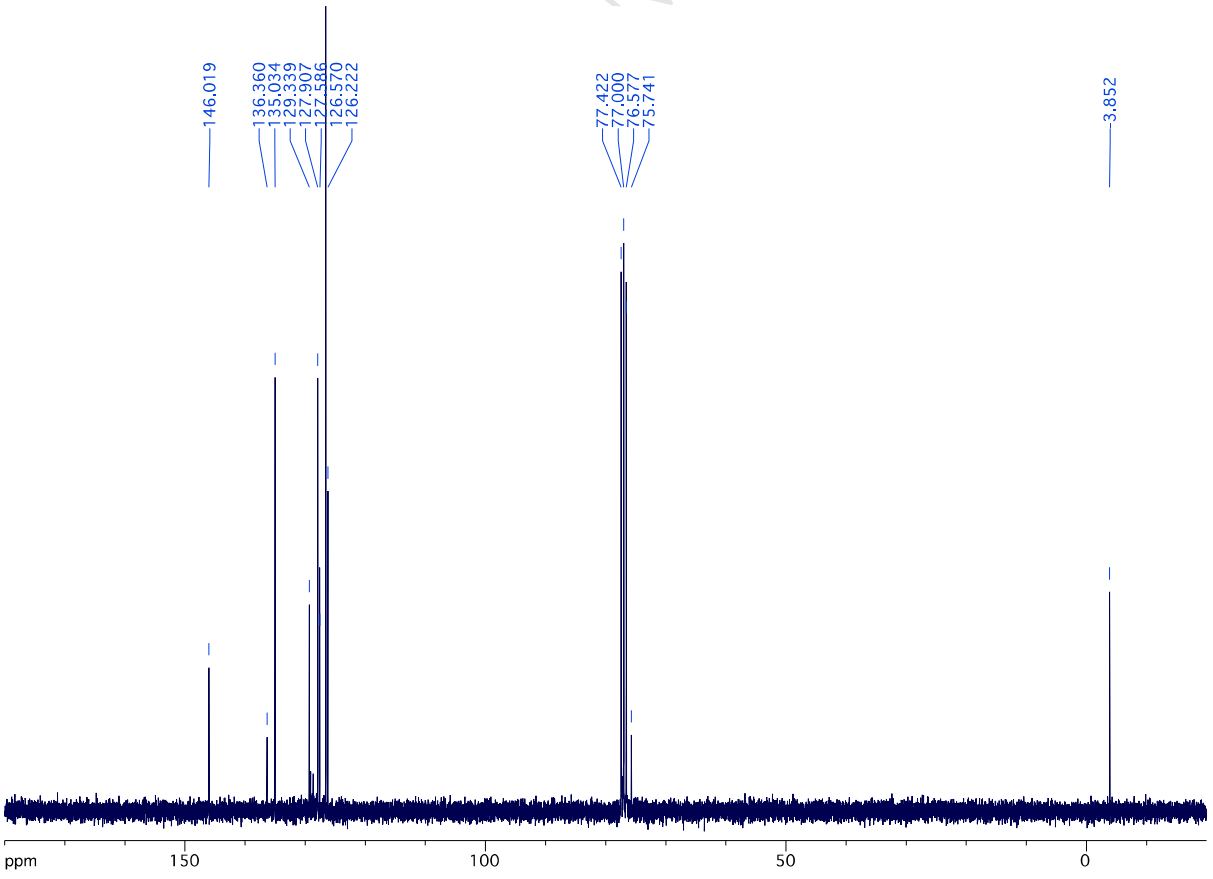
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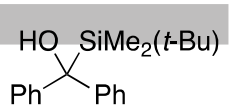
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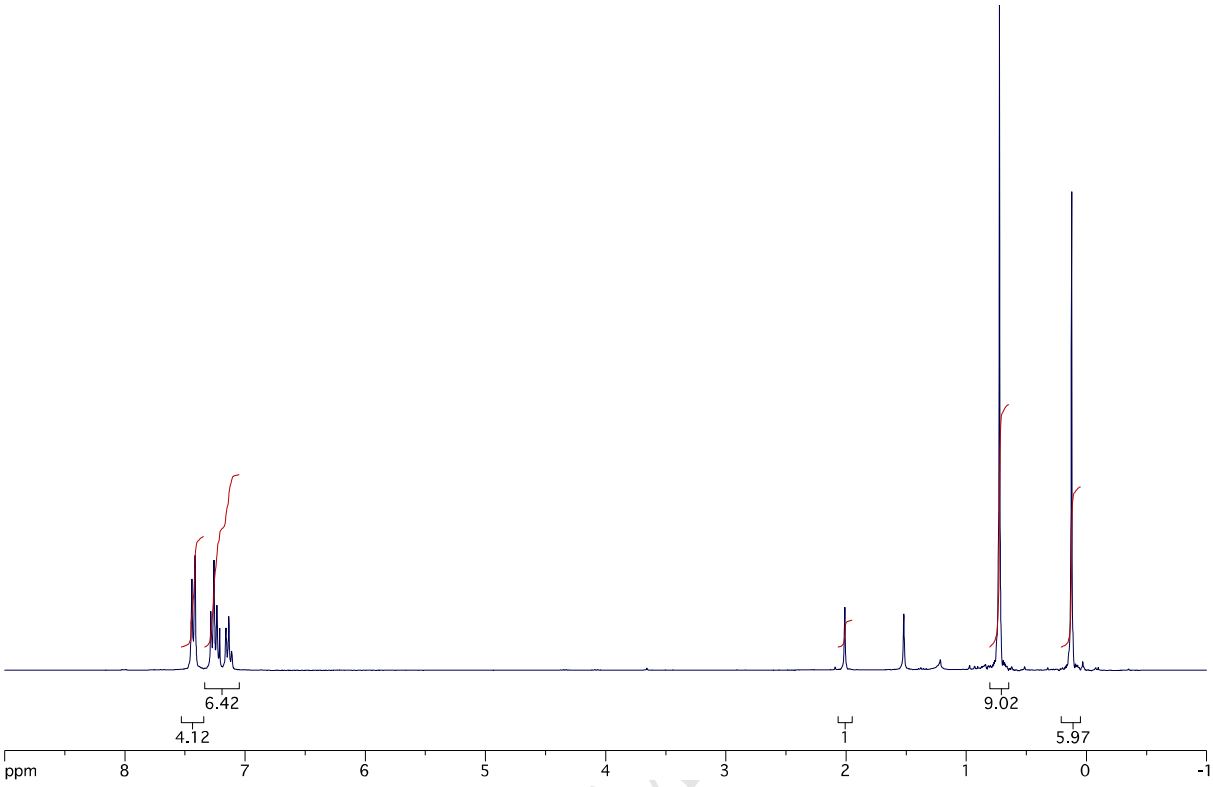
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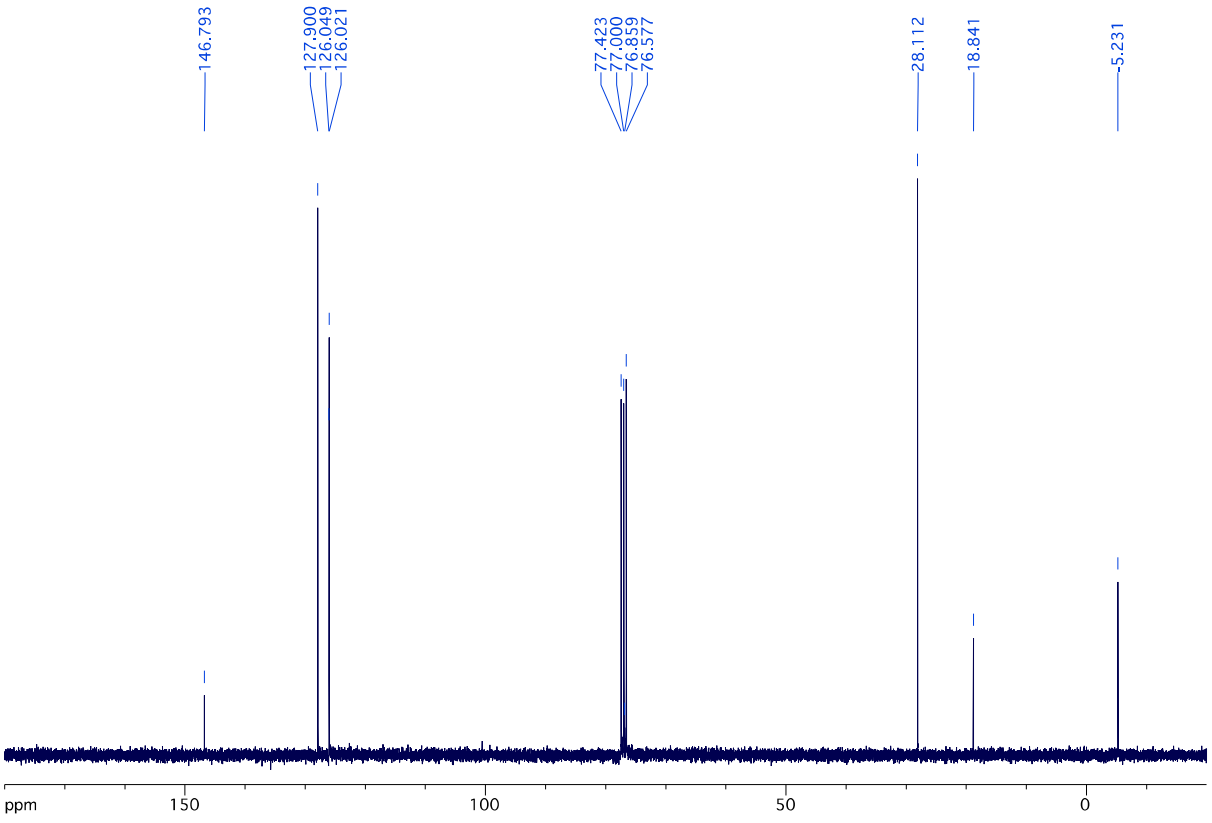
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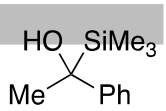
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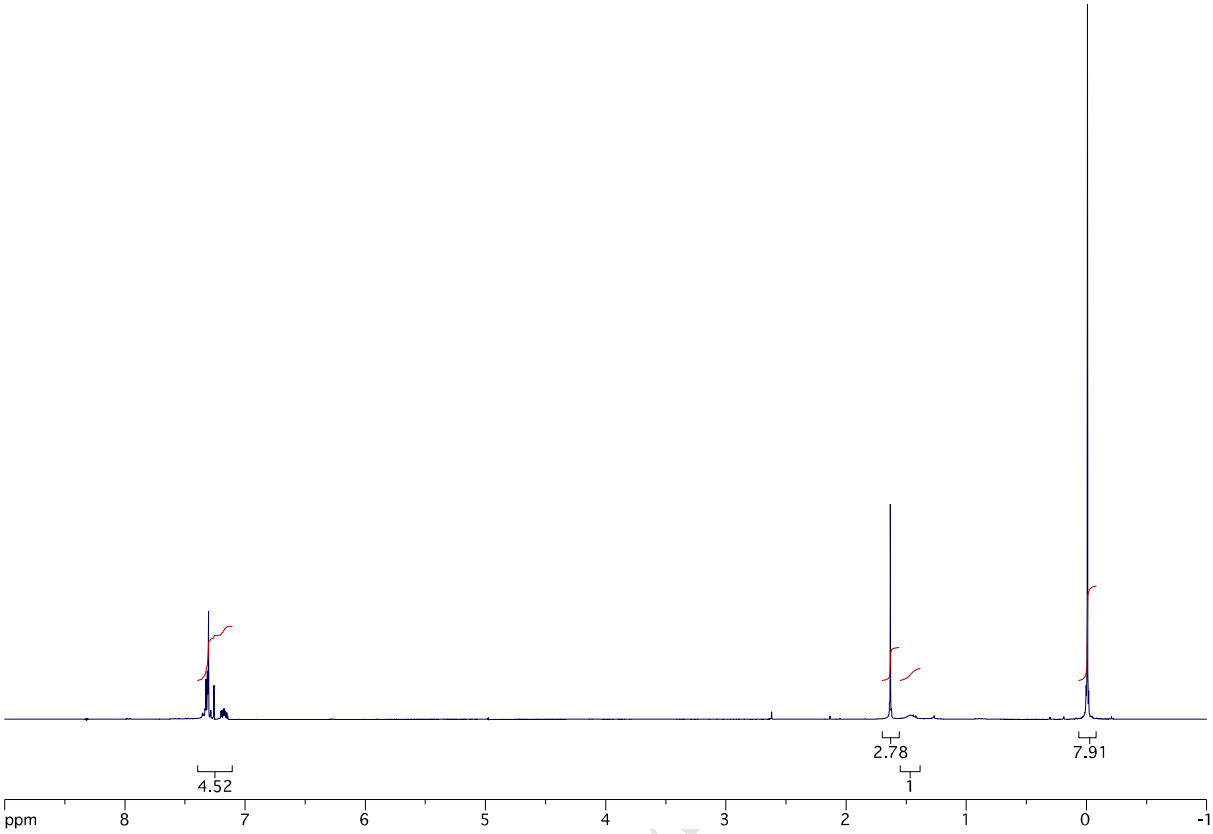
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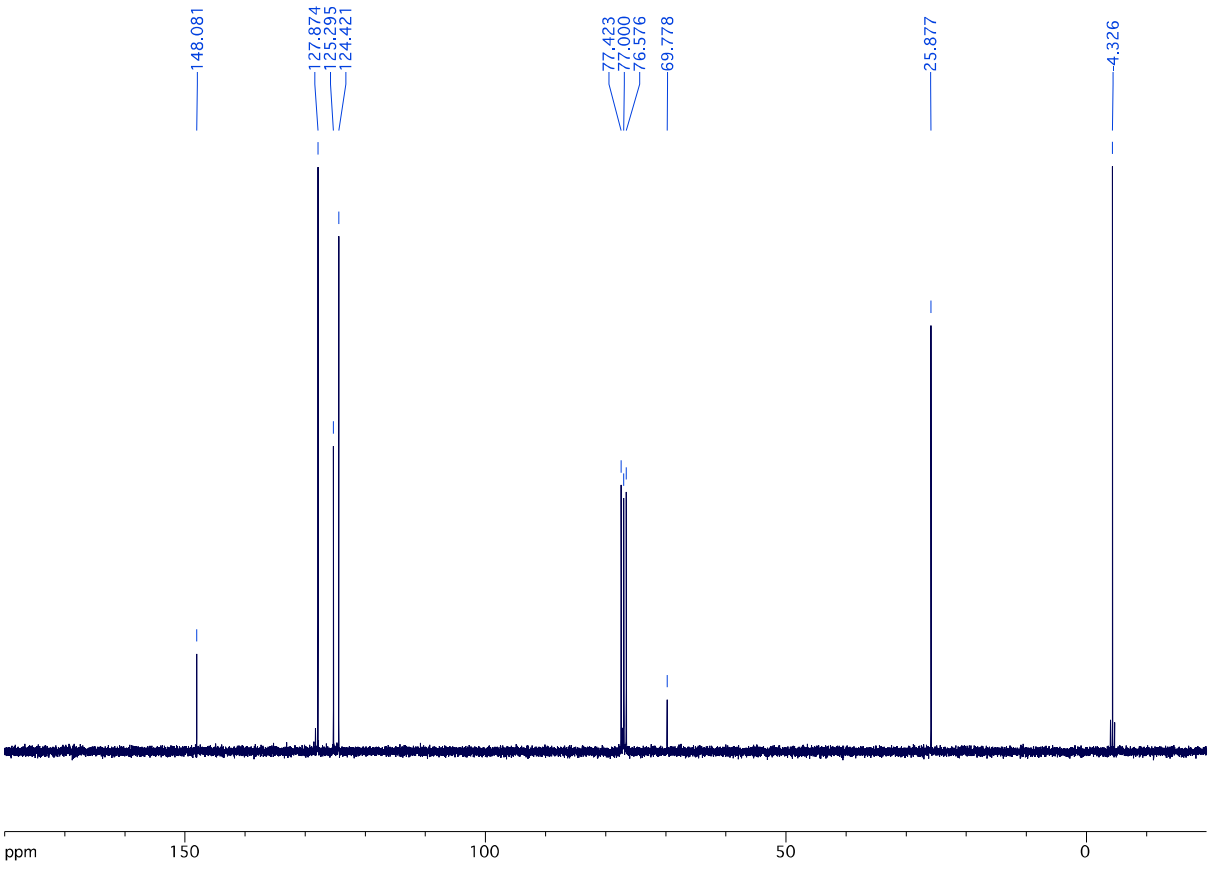
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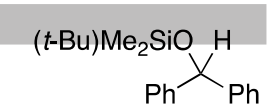
4ca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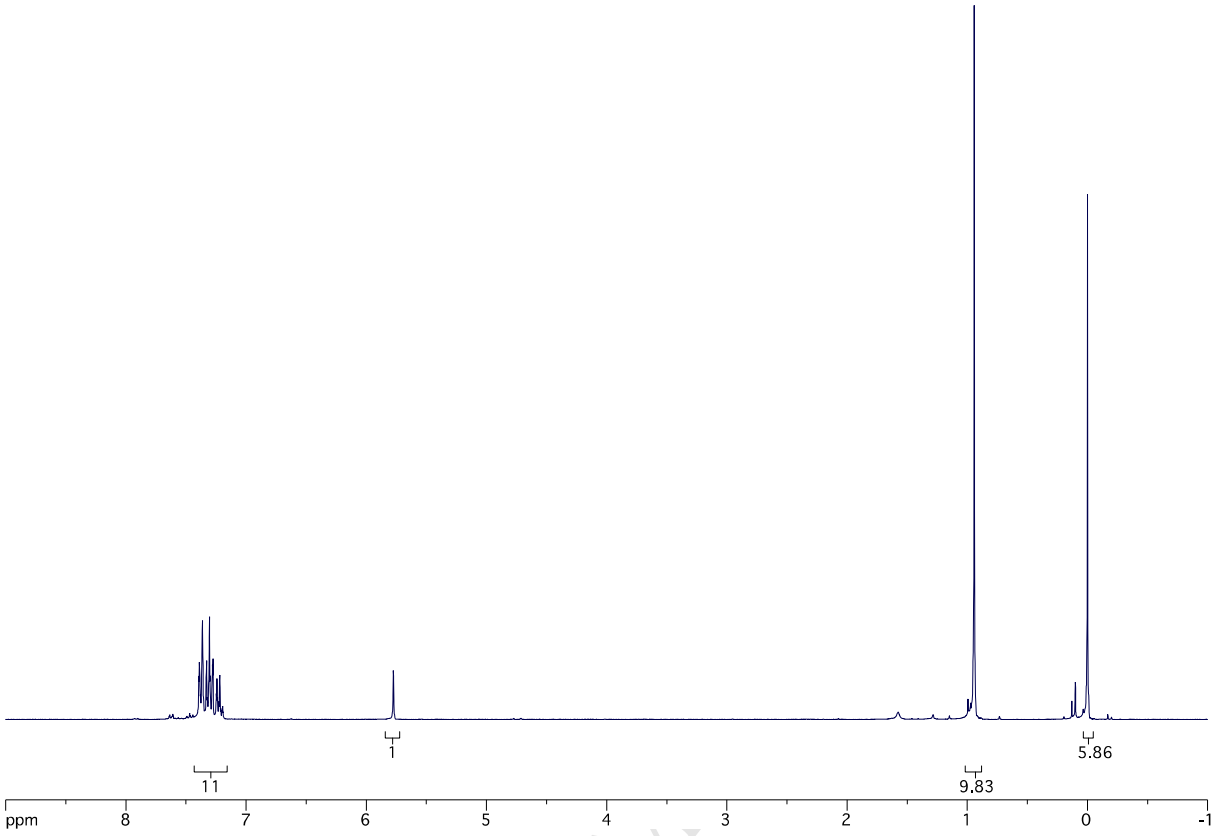
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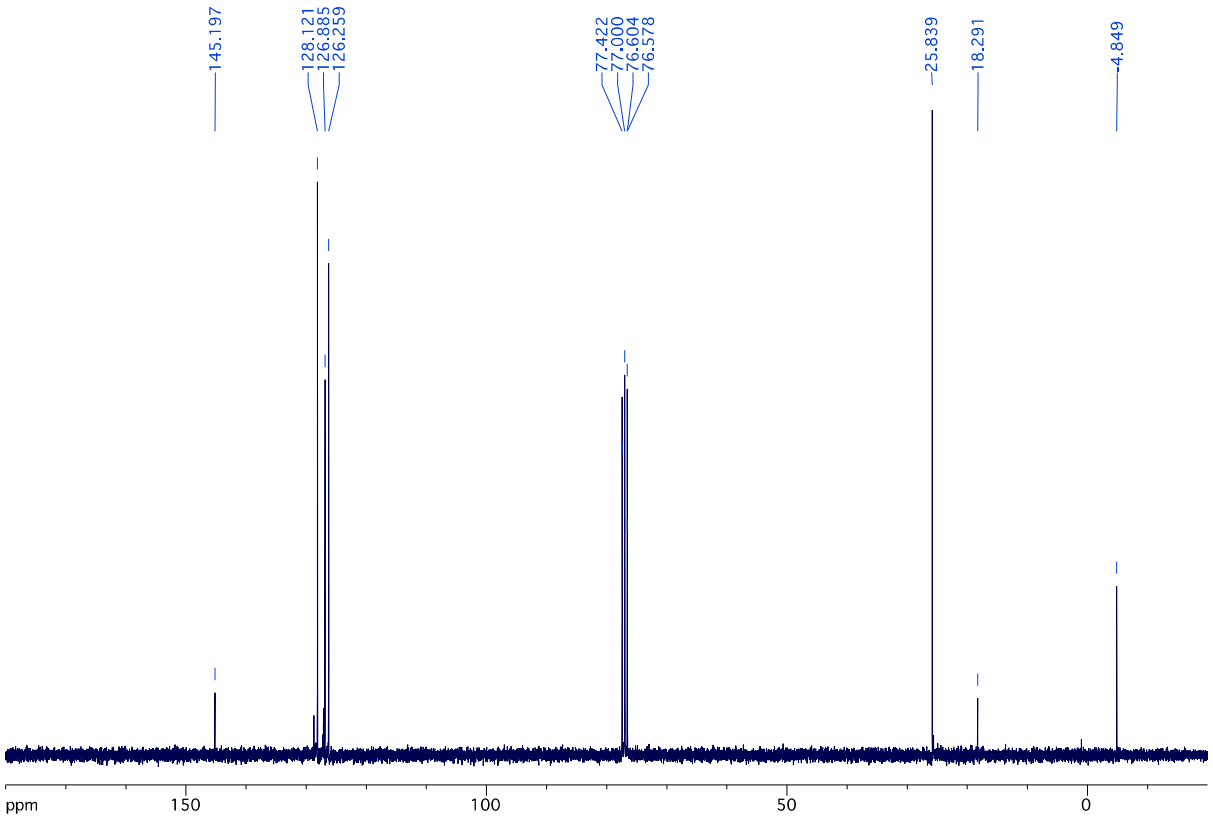
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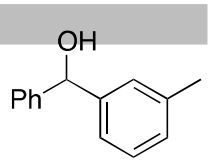
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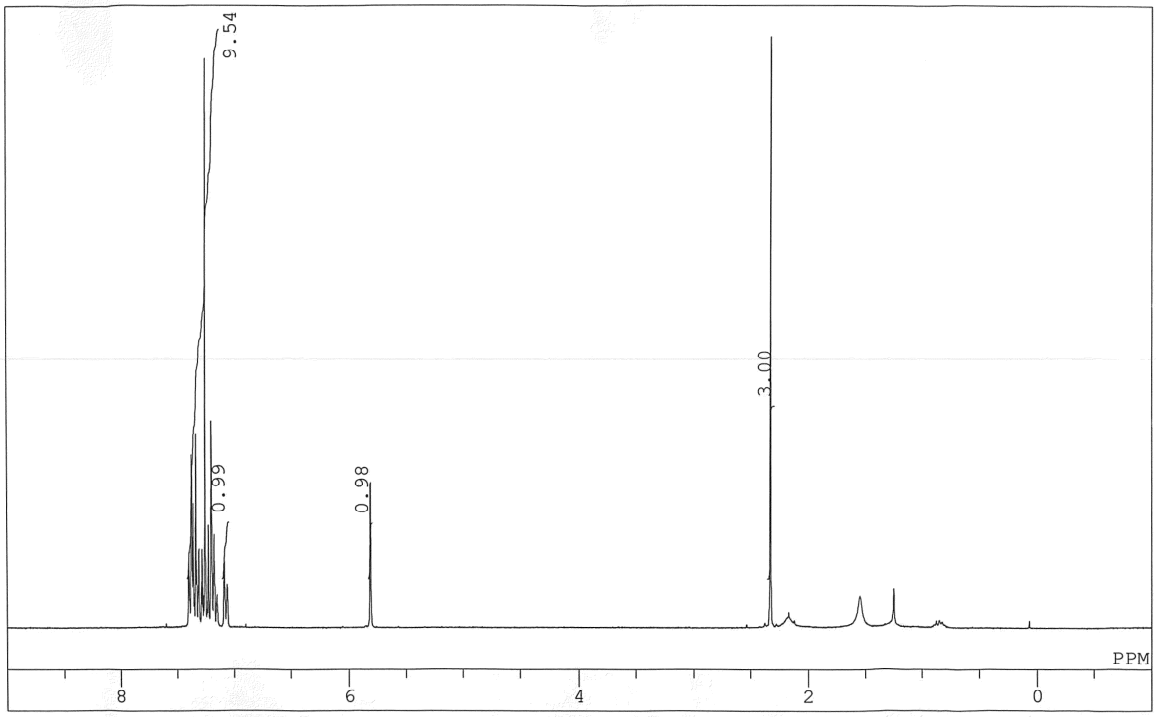
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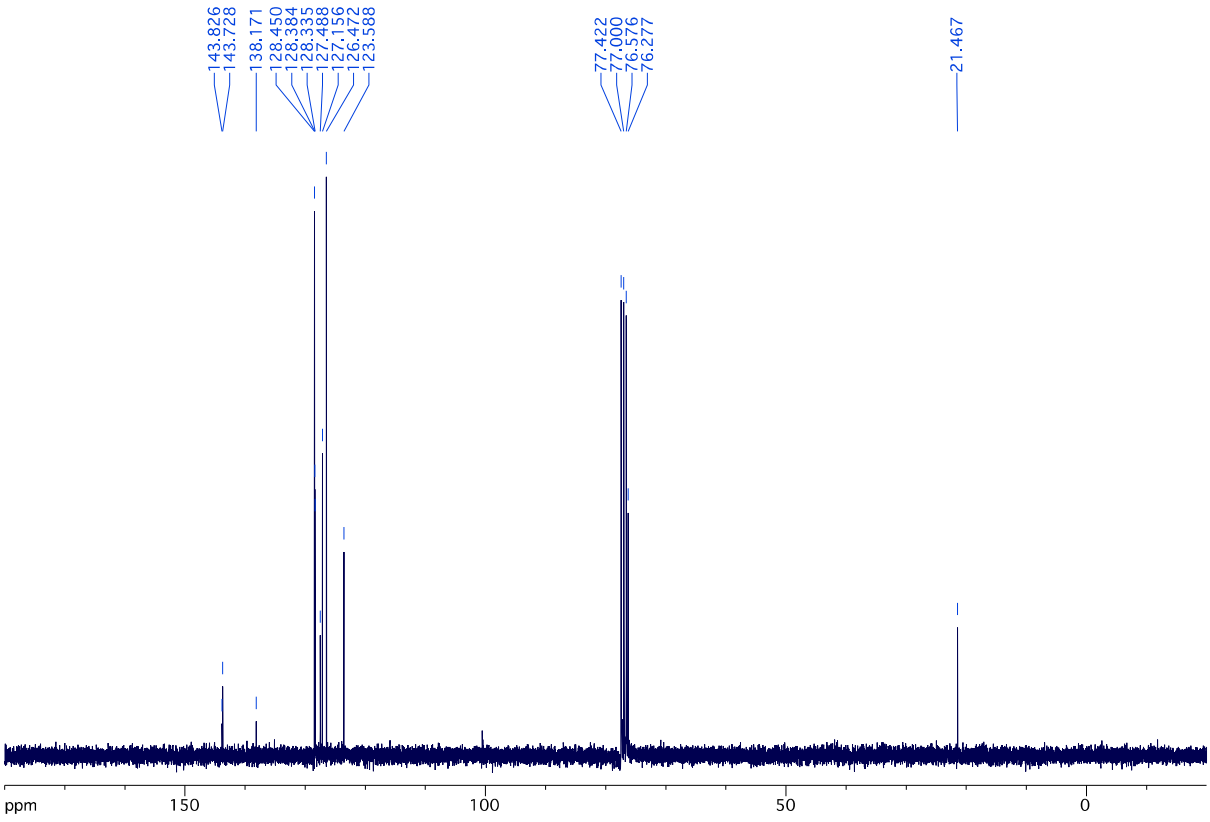
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